Hydrodeoxygenation of oxidized distilled bio-oil for the production of gasoline fuel type

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A B S T R A C T

Distilled and oxidized distilled bio-oils were subjected to 1st-stage mild hydrodeoxygenation and 2nd-stage full hydrodeoxygenation using nickel/silica–alumina catalyst as a means to enhance hydrocarbon yield. Raw bio-oil was treated for hydrodeoxygenation as a control to which to compare study treatments. Following two-stage hydrodeoxygenation, four types of hydrocarbons were mainly comprised of gasoline and had water contents, oxygen contents and total acid numbers of nearly zero and higher heating values of 44–45 MJ/kg. Total hydrocarbon yields for raw bio-oil, oxidized raw bio-oil, distilled bio-oil and oxidized distilled bio-oil were 11.6, 16.2, 12.9 and 20.5 wt.%, respectively. The results indicated that oxidation had the most influence on increasing the yield of gasoline fuel type followed by distillation. Gas chromatography/mass spectrometry characterization showed that 66.0–76.6% of aliphatic hydrocarbons and 19.5–31.6% of aromatic hydrocarbons were the main products for oxidized bio-oils while 35.5–38.7% of aliphatic hydrocarbons and 58.2–63.1% of aromatic hydrocarbons were the main products for non-oxidized bio-oils. Both aliphatic and aromatic hydrocarbons are important components for liquid transportation fuels and chemical products.

1. Introduction

Future predicted shortages in fossil fuel resources and environmental regulations regarding greenhouse gas emissions from fossil fuel combustion have led to great research interest in developing alternatives to fossil fuels [1,2]. Fast pyrolysis of biomass has become the most prevalent method for producing bio-oil, a liquid precursor for the production of heating or transportation fuel [3]. Loblolly pine (*Pinus taeda*) is the major species grown in the southern U.S. Bio-oil conversion facilities built in the south will use small diameter loblolly pine as its biomass source [4,5]. The advantages of bio-oil are its renewability, the abundance of the biomass from which it is produced and the fact that it is carbon neutral, less nitrogen derivatives and almost no sulfur [1,2,6]. However, bio-oil's high oxygen content (45–50 wt.%) – in the form of water (~30 vol.%) and numerous reactive oxygenated functionalities (aldehydes, ketones, acids, phenols, etc.) – is responsible for nearly all of its negative properties, including but not limited to its low higher heating value (HHV) (~17 MJ/kg), low pH (~2.5) and increased viscosity during storage or upon heating [7,8]. These

negative physical and chemical properties [8] hinder both its direct use as a fuel and the fuel conversion process.

Hydrodeoxygenation (HDO) is considered most effective method for bio-oil upgrading using a variety of heterogeneous catalysts in the high pressure of hydrogen [9]. Ni-based catalysts showed high activity for hydrodeoxygenation [10–13]. However, the presence of high water content is harmful to the acid γ-Al$_2$O$_3$ or zeolite supports (dealumination), which are the main supports for petroleum refining catalysts to remove sulfur, oxygen and nitrogen. This water-based oxygen becomes steam vapor during thermo-chemical hydroprocessing and collapses the pores of catalysts [14]. Because of raw bio-oil's thermal instability, it is impossible to apply petroleum distillation methods in its refining. This is because the water content in bio-oil cannot be separated by distillation as the reactive components of bio-oil polymerize with application of heat. It has been shown that co-feeding only 3% of raw pyrolysis oil with vacuum gas oil into a fluid catalytic cracker plugged the feed nozzle because of excessive coke deposition [15]. In addition, aldehydes in the bio-oil undergo homopolymerization, acetalization and oligomerization by reacting with phenols to produce high molecular weight thermoplastic resins by polymerization [7]. Previous research also shows that aldehyde polymerization reactions during HDO are mainly responsible for

catalyst coking and lower hydrocarbon yields [7]. Moreover, the polymerization reaction of aldehydes is the main factor in bio-oil viscosity increase over time (during storage) or upon heating [16]. Since most of the issues during catalytic refining of bio-oil (to hydrocarbons) arise from bio-oil's oxygen in the form of water and reactive functional groups such as aldehydes, minimizing oxygen (by limiting water in bio-oil) and aldehyde content in bio-oil prior to refining tend to produce better results.

Mohan et al. [8] reviewed solvent fractionation methods to fractionate post-production bio-oil into solvent-soluble and solvent insoluble phases, including solvents such as water, methanol, pentane, hexane, ethyl acetate, ether (diethyl ether or ethyl ether), benzene and dichloromethane. Oasmaa et al. [17] applied a model mixture solvent to stabilized the bio-oil. High-pressure thermal treatment [18] was also applied to fractionate bio-oil to water-soluble and water-insoluble organic fractions. But these fractionation methods all depended on the separation of water from bio-oil after the production of whole bio-oil.

Newer methods [19–23] for water separation from bio-oil have been based on fractionation of water from bio-oil organic components during pyrolysis itself. These methods depend on utilization of multiple pyrolysis reactor condensers in which temperature controls the distillation of pyrolysis vapor into individual components based on molecular weight classes. This approach is similar to distillation technology by which the process is mainly dependent on the dew point of the bio-oil components. Selective condensation of fast pyrolysis vapors was also achieved using a liquid spray (bio-oil [24] or water [25]) to quench and fractionate pyrolysis vapors. The distillation of water from pyrolysis vapor during pyrolysis vapor condensation itself will limit bio-oil processing difficulties to some extent and also eliminate additional step for water separation. The organic fractions with lower water content have been shown to be catalyzed more effectively to improve bio-oil properties and produce hydrocarbons [26,27].

As aforementioned, minimizing reactive functional groups such as aldehydes in bio-oil is also essential for effective bio-oil refining. Gayubo et al. [16] used model compound studies to compare the reactivity of aldehydes (acetaldehyde) and acids (acetic acid) and found that acids are thermally more stable and produced less thermal coke compared to aldehydes. Reduction of aldehydes to 3.6 wt.% was advisable to avoid heavy coke. Therefore, converting aldehydes in bio-oil to carboxylic acids may limit the formation of thermal coke while processing at high temperatures. Aldehydes can be converted to acids by ozone oxidation or to esters in the presence of alcohols [28,29]. Xu et al. [30] improved bio-oil properties and removed water by ozonation and esterification. Tanneru et al. [4] applied ozone/H_2O_2 oxidation to convert aldehydes in raw bio-oil to acids which were esterified with butanol to produce a high-yield boiler fuel in the presence of nickel/silica–alumina catalysts. Tanneru & Steele [12] also found that partial nickel/silica–alumina catalyzed HDO of bio-oil oxidized with oxone/H_2O_2 lowered char production as well as reduced hydrogen consumption while producing 30.5% higher organic fraction yield compared to partial HDO of raw bio-oil.

Research on HDO of low-water bio-oil has been performed [31]; no research is available on HDO of distilled bio-oil and oxidized distilled bio-oil. While distilled bio-oil has low water content, it also differs likely from other low-water bio-oils in the chemical species collected during distillation. In addition, HDO of oxidized low water bio-oil or distilled bio-oil has not been reported. The objective of this research was to determine if an in situ pyrolysis vapor distillation product or its oxidized form would produce high yield of gasoline fuel type. Comparing the chemical species distribution of the hydrocarbons produced by distillation and oxidation was also an objective.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

Nickel/silica–alumina catalyst (∼65 wt.% nickel, ∼10 wt.% silica, 10 wt.% alumina, powder, a surface area of 190 m^2/g) was purchased from Alfa Aesar (U.S.). Hydrogen and helium gases were supplied by NexAir (U.S.). Hydrogen peroxide (30 wt.% solution in water, Certified ACS 30.0–32.0%), isopropanol (99.9%, HPLC Grade), dichloromethane (Stabilized/Certified ACS), methanol (Stabilized/Certified ACS) and oxone were purchased from Fisher Scientific. All chemicals were used without further purification.

2.1.2. Distilled bio-oil and bio-oil production

Loblolly pine was ground and sieved to a particle size range of 0.5–4 mm and then oven-dried to a moisture content below 5 vol.%. Fig. 1 shows a schematic of the fractionating pyrolysis reactor employed in this study. The different segments of the reactor can be found by reference to Fig. 1 and Table 1. The pyrolysis operation began with pine biomass poured into a feed hopper (1) and transferred via a motorized auger (2) to a rotary airlock valve (3). A nitrogen purge (4) of 1 scfm was introduced above and below the rotary airlock valve. Along with the nitrogen purge (4), the rotary airlock valve (3) prevented oxygen from entering the pyrolysis reactor and pyrolysis vapors from exiting the pyrolysis reactor while feeding biomass into the reactor. A motorized auger (6) inside the pyrolysis reactor pipe (5) transferred the biomass through a heated zone of 450 °C. Ceramic band heaters (8) around the outside of the pyrolysis reactor pipe (5) provided heat for pyrolysis while thermocouples (9) monitored the temperature inside the pyrolysis reactor pipe (5). While in the heated zone, biomass was converted into char and vapor and continued to be transferred through the pyrolysis reactor pipe (5) and dropped into the char collection vessel by controlling the char valve (10). The non-condensable gases (18) from condenser 4 (15) entered a gas flow meter (17) before being emitted to atmosphere. Pyrolysis gases exited the pyrolysis reactor pipe (5) through the exit gas pipe (11) and into water cooled condenser 1 (12), condenser 2 (13), condenser 3 (14) and condenser 4 (15). Once the pyrolysis gases were condensed, bio-oil drained to the bottom of each condenser and was collected through bio-oil collection ports (16).

To obtain distilled bio-oil, the bio-oil aqueous fraction vapors tended to be condensed in the second condenser as this condenser temperature was maintained below the water vaporization temperature. The bio-oil organic fractions tended to be condensed in condensers 1, 3, 4. Liquid condensates were collected from the exits of the first, third and fourth condensers and combined to be analyzed as the distilled bio-oil (DB) study specimen. Raw bio-oil (RBO) was produced by the same methods described in the literature [12].

2.2. Methods

2.2.1. Oxidation of RBO and DB

All bio-oil oxidation treatments were performed in a stainless steel, high-pressure 1.8 L Parr batch autoclave reactor equipped with an overhead magnetic stirrer, a maximum pressure capacity of 5000 psig and maximum temperature capacity of 500 °C. Oxidation reactions of 500 g of RBO or DB were performed with 50 g of hydrogen peroxide and 25 g of oxone while stirring for 90 min at ambient temperature and pressure [4]. The oxidized products were termed as oxidized raw bio-oil (ORBO) and oxidized distilled bio-oil (ODB).